

Appendix D

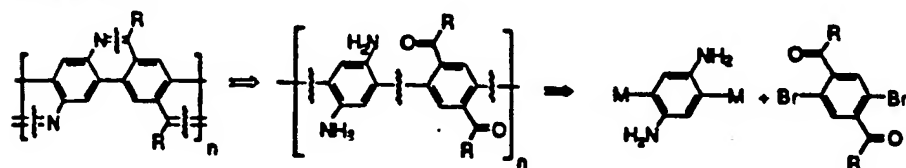
Improved Route to Bridged Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended π -Conjugation

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Poly(*p*-phenylene) (PPP), a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist between the consecutive aryl units due to ortho hydrogen interactions.¹ Attempts to enhance the solubility by substitution of the rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).¹ We recently described a route to soluble ladder PPP derivatives.² Here we describe an improved synthetic route to the monomers as well as an aryl-substituted ladder PPP derivative.³

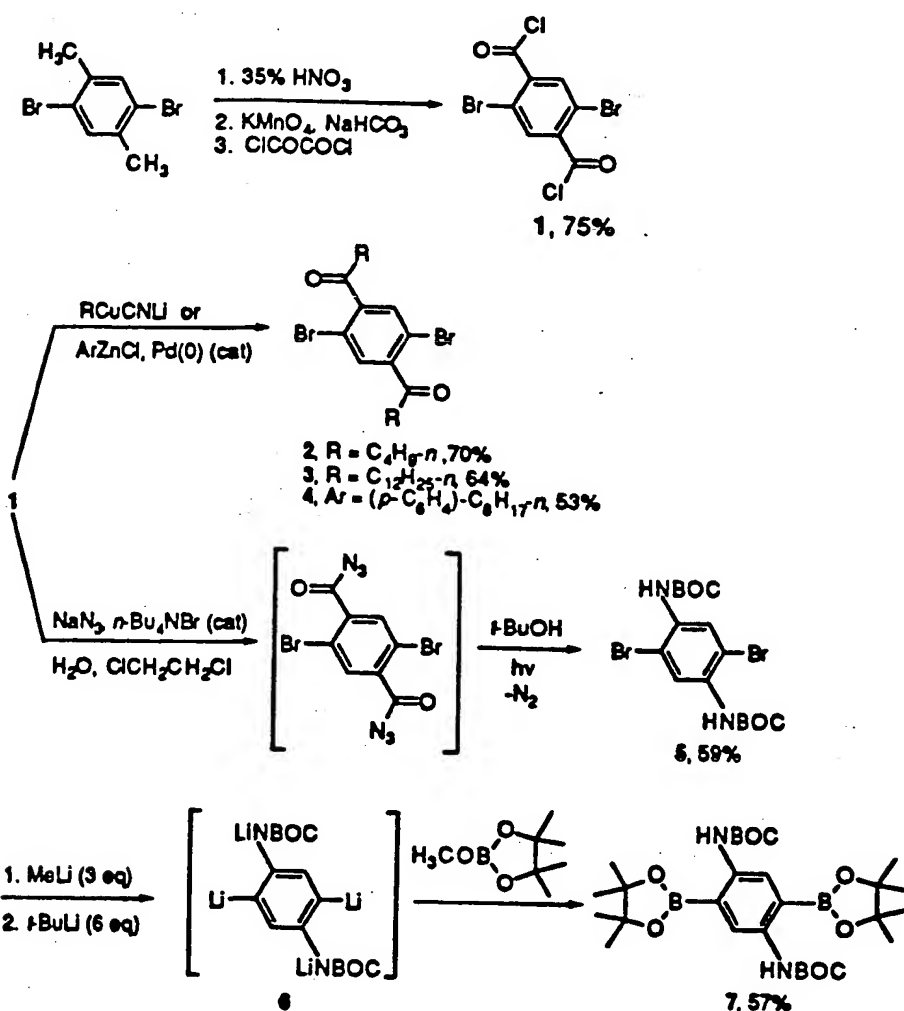
Our retrosynthetic approach involved two key steps (Scheme I, M = metal). First, imine cleavage to the

Scheme I



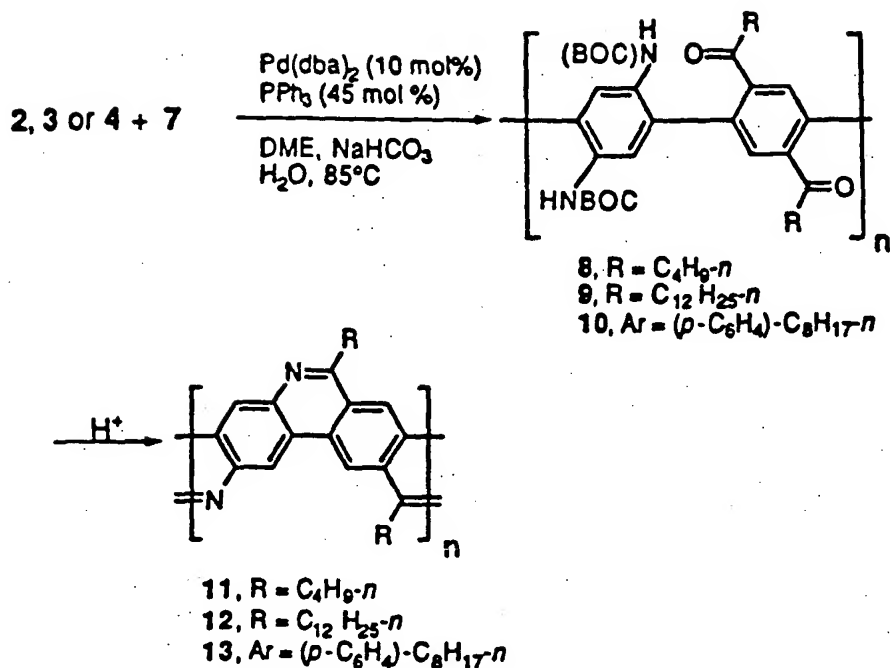
ketoamine functionalized PPP, and second, bond cleavage to the two arene systems shown. Since Pd(0)-catalyzed oxidative addition reactions are facilitated with electron deficient ring systems,⁴ we chose to keep the halides on the ketoaromatic portion.

After several nearly quantitative model reactions, we synthesized the two key monomers needed for the desired AB-type step growth polymerization. Dibromoxylene was oxidized by a two-step procedure⁵ which was superior to the one step Co(OAc)₂ procedure² described previously. The route described here is an improvement over our former approach in that the same dibromobis(acid chloride) (1) can be used for the synthesis of both the A and B monomer units. Conversion of 1 to the diketone was



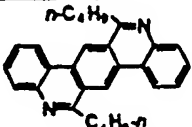
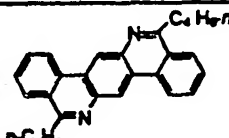
While 5 was nearly insoluble in ether at 0°C, it could be tetralithiated in ether to form a soluble intermediate 6 in almost quantitative yield (checked by addition of TMSCl and isolation of the arylbis(silane) after aqueous work-up). Treatment of 6 with methyl pinacol borate afforded the monomer 7 which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase (silica gel or neutral alumina caused rapid decomposition of the intermediate) and CH₂Cl₂ as the eluant followed by recrystallized to form pure 7.

Reaction of 2, 3, or 4 with 7, in the presence of a Pd(0) catalyst, yielded the soluble polymers 8, 9, and 10, respectively, from which size exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (8: 63% yield after fractional precipitation, $M_n = 9,850$ with $M_w/M_n = 1.85$; 9: 97% yield after fractional precipitation, $M_n = 28,400$ with $M_w/M_n = 3.70$; 10: 80% yield after fractional precipitation, $M_n = 18,500$ with $M_w/M_n = 2.75$). Upon exposure of 8, 9, or 10 to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded 11 (90% yield), 12 (97% yield), and 13 (90% yield), respectively.⁸ All stretches for the ketone, carbamate, and amine in 8, 9, and 10 were absent in the FTIR spectrum of the planar polymers.



The optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of 8 to 11, 9 to 12, and 10 to 13); an observation consistent with the proposed ladder formation (Table I). The UV-vis spectrum of 13 in a CH₂Cl₂/trifluoroacetic acid (3/2) mixture is shown in Figure 1. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers,⁹ oligo(*p*-phenylenes), and PPP.¹⁰

Table I. Optical Absorption Data

Compound	λ in solution (nm) ^a	λ of solid (nm) ^a
8	CH ₂ Cl ₂ : <u>250</u> , 306 (sh)	<u>248</u> , 308 ^b
9	CH ₂ Cl ₂ : <u>250</u> , 388	<u>250</u> , 398 ^b
10	CH ₂ Cl ₂ : <u>254</u>	<u>254</u>
11	CH ₂ Cl ₂ /TFA: 374, <u>396</u> , 426 (sh), 514, 520 (ed) ^c	-----
12	CH ₂ Cl ₂ /TFA: 376, <u>400</u> , 428, 478, 516, 530 (ed) ^c	<u>463-490</u> ^d
13	CH ₂ Cl ₂ /TFA: 380, <u>402</u> , 458, 506, 549 ^c	-----
	CH ₂ Cl ₂ : <u>300</u> (ref 9)	-----
	CH ₂ Cl ₂ : <u>294</u> (ref 9)	-----
<i>p</i> -sexiphenylene	CHCl ₃ : <u>318</u> (ref 10)	-----
PPP (calcd infinite <i>M_n</i>)	<u>344</u> (ref 10)	-----

^a λ_{\max} is underlined, (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{\max} intensity. ^bAlso a strong carbonyl absorption at 196 nm. ^cSpectrum recorded on the acid solublized, therefore, multiprotonated system. ^dThese λ_{\max} values were recorded on a series of four different polymer samples of 9 in order to insure their reproducibility.¹¹

Figure 1. UV-vis spectrum of 13 in a CH₂Cl₂/TFA (3/2) mixture

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References and Notes

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- (8) 8: Anal. calc'd for $(C_{32}H_{42}N_2O_6)_n$: C, 69.79; H, 7.69; N, 5.07. Found: C, 70.55; H, 7.25; Br, <0.5; N, 5.13. 9: Anal. calc'd for $(C_{48}H_{74}N_2O_6)_n$: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.99; H, 9.40; Br, <0.5; N, 3.55. 11: Anal. calc'd for $(C_{22}H_{22}N_2)_n$: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56. 12: Anal. calc'd for $(C_{38}H_{54}N_2)_n$: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.
- (9) The planar trimers were prepared during our model studies for the polymerizations described here using Pd-catalyzed couplings.
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